

MICROEMULSION-MEDIATED SYNTHESIS OF NANOSIZE MOLYBDENUM SULFIDE COAL LIQUEFACTION CATALYSTS

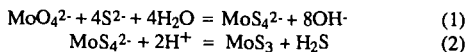
E. Boakye, N. Vaidyanathan, L.R. Radovic and K. Osseo-Asare
Department of Materials Science and Engineering
The Pennsylvania State University, University Park, PA 16802

INTRODUCTION

In heterogeneous catalysis, the size of the catalyst is of considerable importance in that the extent of reaction is often inversely proportional to the particle size of the catalyst. As a consequence, various methods have been used to synthesize particles of large specific surface area for catalysis applications (1-3). Most of these methods are based on hydrocolloids (1) and aerosols (2). Recently microemulsion-based synthesis is also attracting attention (3). Haruta et al. (1) prepared molybdenum sulfide particles in the micrometer size range by reacting ammonium molybdate and thioacetamide. Different particle sizes were obtained by varying the pH. In the preparation of iron sulfide catalysts for coal liquefaction, Andres et al. (2) used an aerosol-based method to synthesize iron oxide particles which were used *in situ* with carbon disulfide to liquefy coal. The liquefaction yield was found to be inversely proportional to the particle size. The synthesis of nanosize particles using inverse microemulsions has been reported for a variety of materials (4,5), among which are the hydrogenation catalysts nickel and cobalt borides (3), and platinum-group metals (6,7). Others worth noting are cadmium sulfide (4,8-10), copper, lead, and indium sulfides (9,11), cadmium selenide (12), silica (5), and silver halide (13,14). In this communication a microemulsion-based method for the synthesis of molybdenum sulfide nanosize particles is reported for the first time. This material is currently under active investigation as a potential coal liquefaction catalyst (15).

An inverse microemulsion is a thermodynamically stable, optically isotropic dispersion of microdrops of water in an external oil phase stabilized by a surfactant (16-18). The microemulsion systems used in this study are: polyoxyethylene(5)nonylphenylether (NP-5)/cyclohexane/water and NP-5/tetralin/benzyl alcohol/water. The latter system was used previously in this laboratory as a medium for the synthesis of silica nanoparticles (5). In these systems the water molecules interact with the hydrophilic portion of the surfactant molecules via hydrogen bonding to form inverse micelles. The addition of more water molecules results in the formation of swollen inverse micelles, often referred to as inverse microemulsions. The water pools inside the inverse micelles vary in size depending on the water-to-surfactant molar ratio (R) and are in the size range of 3-30 nm (16-18). Due to the cage-like nature of the water pools, particle growth is limited when particle precipitation is effected in them. Advantage has been taken of this unique property of inverse microemulsions to synthesize nanosize molybdenum sulfide particles in the size range 10-150 nm. The large surface area available on these nanoparticles results in a high yield of hexane-soluble oils when coal is liquefied (15).

The chemistry pertaining to the formation of molybdenum sulfide is summarized below:



The following thiomolybdate species are formed when ammonium molybdate is reacted with the sulfide ligand at a pH of 3-11: $\text{MoO}_3\text{S}^{2-}$, $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-} . Extensive formation of the tetrathiomolybdate ion depends on the sulfur-to-molybdenum ratio and on solution pH (19-22). As can be seen from Equation 2, molybdenum sulfide forms when an acid is added to tetrathiomolybdate species.

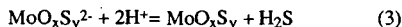
EXPERIMENTAL SECTION

The following chemicals were obtained from Aldrich: the non-ionic surfactant polyoxyethylene(5)nonylphenylether (NP-5), ammonium tetrathiomolybdate (99.97%), cyclohexane (99%) and 1,2,3,4-tetrahydronaphthalene (tetralin). Before use cyclohexane and tetralin were dried with molecular sieves. The inverse microemulsions NP-5/cyclohexane/water and NP-5/tetralin/benzyl alcohol/water were prepared at room temperature by adding 10% sulfuric acid to a solution of 0.134 M NP-5/cyclohexane and 0.4 M NP-5/tetralin/benzyl alcohol, respectively. The acid-solubilized microemulsion was deoxygenated by bubbling nitrogen gas through it for 20 min. This procedure was followed by adding 1×10^{-3} M and 1×10^{-2} M ammonium tetrathiomolybdate to the 0.134 M NP-5/cyclohexane and 0.4 M NP-5/tetralin/benzyl alcohol, respectively. Nitrogen was further bubbled while the molybdenum sulfide was being precipitated according to Equation 2. For the NP-5/cyclohexane/water microemulsion the concentration of the reactant species was constant with respect to the total microemulsion. On the other hand, in the case of the NP-5/tetralin/benzyl alcohol/water microemulsion, the concentration of the reactant species was maintained at a constant value with respect to the water pools.

Ultraviolet/visible spectra were obtained with a Hewlett Packard 84151A diode array spectrophotometer. Samples for transmission electron microscopy were prepared by directly dropping a very small amount of molybdenum sulfide dispersion on carbon-coated copper grids and drying at room temperature. Prior to sample extraction, each sample bottle was sonicated for 1 min. Particle sizes were determined with a Philips 420 transmission electron microscope operating at 120 kV with a resolution of about 0.6 nm. The diameters of at least 300 particles were measured for each sample to obtain an average particle diameter and standard deviation.

RESULTS AND DISCUSSION

Molybdenum sulfide nanoparticles have been synthesized successfully in the following microemulsion systems: NP-5/cyclohexane/water and NP-5/tetralin/benzyl alcohol/water. Figures 1 and 2, respectively, refer to the ultraviolet/visible absorption spectra of ammonium tetrathiomolybdate and molybdenum sulfide particles in a 0.1 M NP-5/cyclohexane microemulsion system. The microemulsions represented in these two figures contained equal amounts of 1.0×10^{-3} M ammonium tetrathiomolybdate, except that the microemulsion in Figure 2 contained 10% sulfuric acid. These two figures are different in that the absorption peaks for MoS_4^{2-} and $\text{MoO}_2\text{S}_2^{2-}$ (23) are absent in Figure 2 while a peak with an onset wavelength of about 350 nm appears. The disappearance of the peaks for the thiomolybdate species suggests that conversion (i.e., Equations 2 and 3) took place in the inverse microemulsion when the thiomolybdate species found themselves in the same inverse micelle with protons:



NP-5/Cyclohexane/Water. Figures 3 and 4, respectively, present TEM micrographs of molybdenum sulfide particles in the 0.134 M NP-5/cyclohexane/water microemulsion system and a plot of water-to-surfactant molar ratio (R) versus the average particle diameter. The average particle diameter decreases with R to a value of 2 and then increases with R. This trend may be rationalized in terms of nucleation and growth phenomena (3,4,14). The process of particle formation from dissolved ions can be represented in the following order: Ions \rightarrow Monomer \rightarrow Nuclei \rightarrow Particles (24). After a stable nucleus is formed, it can grow by the following growth processes: (a) Incorporation of ions and monomers in solution into already formed nuclei (3), and (b) aggregation of primary particles or nuclei to form bigger particles (4,14).

The nucleation and initial growth of particles takes place in the inverse micelles through collision, fusion and splitting of inverse micelles. In order to form a stable nucleus, a cluster containing a critical number of monomers (N_c) must form. A useful

parameter in this connection is that of the ion occupancy number, i.e., the number of reactant species in an inverse micelle. A nucleus is formed if the ion occupancy number is greater than N_c . As the water-to-surfactant molar ratio is decreased, the surfactant aggregation number decreases (25,26) and the micellar concentration increases. This corresponds to a decrease in the ion occupancy number because the concentrations of the reactant species (MoS_4^{2-} and H^+) in the microemulsion are constant. For low R values, relatively fewer water cores will therefore contain the minimum number of ions required to form a nucleus. As a result, the ions left over after the nucleation process are relatively large. These ions will be incorporated into the already formed nuclei via inter- and intramicellar communication and will contribute to growth, leading to large particles, as demonstrated by the top left side of Figure 4.

As R increases, the aggregation number increases, the micellar concentration decreases, and therefore the ion occupancy number increases. The observed decrease in particle size with increase in R below $R=2$ can be attributed to the increase in ion occupancy number with R . From nucleation theory, the greater the number of nuclei in the inverse microemulsion, the smaller the particle size. This is because there will be relatively few ions left over after the nucleation process, i.e., almost all the ions are used up in the nucleation process.

At $R>2$ the proportion of water in the microemulsion is relatively large, hence the aggregation number is large and the concentration of swollen inverse micelles (water pools) is significantly reduced. As a first approximation, if only one nucleus forms in a water pool, then the decrease in the number of water pools corresponds to a decrease in the number of nuclei that transform into primary particles; hence, there is an increase in the concentration of excess ions which are not utilized in the nuclei formation and are therefore available for particle growth.

NP-5/Tetralin/Benzyl Alcohol/Water. The microemulsion system consisting of NP-5/tetralin/benzyl alcohol has an inherent advantage for coal liquefaction in that tetralin is an excellent process solvent and hence the need to harvest the particles from the synthetic medium can be avoided. Figures 5 and 6 represent respectively the TEM micrograph and a plot of the average particle size versus the water-to-surfactant molar ratio (R) in the 0.4 M NP-5/tetralin/benzyl alcohol/water microemulsion. The particle size decreases with increasing R to a value of 2, and then increases with R . The trend in Figure 6 can be explained in an analogous manner to that observed in Figure 4. In this system two factors, i.e., the water-to-surfactant molar ratio (R) and reactant concentration, increased the ion occupancy number simultaneously.

CONCLUSIONS

Nanosize molybdenum sulfide particles have been synthesized in 0.134 M NP-5/cyclohexane/water and 0.4 M NP-5/tetralin/benzyl alcohol/water microemulsions. The particle size varies with the water-to-surfactant molar ratio. The synthesis of molybdenum sulfide using tetralin as a solvent has potentially important technological applications since catalyst preparation does not involve particle harvesting. Advantage can be taken of the variation of particle size with the water-to-surfactant molar ratio (R) to make particles of desired sizes for coal liquefaction. It should be mentioned that liquefaction tests conducted so far have given high yields of hexane-soluble oils and the yield of oils has been found to be inversely proportional to particle size (15).

ACKNOWLEDGEMENT

This work is being supported by the Department of Energy, Contract No. DE-AC22-90PC90054.

REFERENCES

1. M. Haruta, J. Lemaitre, F. Delannay and B. Delmon, *J. Coll. Interf. Sci.* **101**, 59 (1984).
2. M. Andres, H. Charcosset, P. Chiche, L. Davignon, G. Djega-Mariadassou, J.P. Joly and S. Pregermain, *Fuel* **62**, 69 (1983).
3. I. Ravet, J.B. Nagy and E.G. Derouane, in "Preparation of Catalysts IV," Elsevier (B. Delmon, P. Grange, P.A. Jacobs and G. Poncelet, Eds.), 1987, p. 505.
4. T.I. Towey, A. Khan-Lodhi and B.H. Robinson, *J. Chem Soc. Faraday Trans.* **86**, 3757 (1990).
5. K. Osseo-Asare and F.J. Arriagada, *Coll. Surf.* **50**, 321 (1990).
6. M. Boutonnet, J. Kizling and P. Stenius, *Coll. Surf.* **5**, 209 (1982).
7. A. Claerbout and J.B. Nagy, in "Preparation of Catalysts V," Elsevier (G. Poncelet, P.A. Jacobs, P. Grange and B. Delmon, Eds.), 1991, p. 705.
8. C. Petit and M.P. Pileni, *J. Phys. Chem.* **98**, 2282 (1988).
9. P. Lianos and J.K. Thomas, *Mater. Sci. Forum* **25-26**, 369 (1988).
10. S. Modes and P. Lianos, *J. Phys Chem.* **93**, 5854 (1989).
11. T. Dannhauser, M. O'Neil, K. Johansson, D. Whitten and G. McLendon, *J. Phys. Chem.* **90**, 6074 (1986).
12. M.L. Steingerwald, A.P. Alivisatos, J.M. Gibson, T.D. Harris, R. Kortan, A.J. Muller, A.M. Thayer, T.M. Duncan, D.C. Douglas and L.E. Brus, *J. Am. Chem. Soc.* **110**, 3046 (1988).
13. M. Dvolaitzky, R. Ober, C. Taupin, R. Anthore, X. Auvray, C. Petipas and C. Williams, *J. Dispers. Sci. Technol.* **4**, 29 (1988).
14. M.I. Hou and D.O. Shah, in "Interfacial Phenomena in Biotechnology and Materials Processing" (Y. Attia, B.M. Moudhil and S. Chander, Eds.), Elsevier, 1988, p. 443.
15. N. Vaidyanathan, E. Boakye, K. Osseo-Asare and L.R. Radovic, *ACS Preprints, Fuel Chem. Div.* (San Francisco, 1992), in press.
16. J.H. Fendler, *Chem. Rev.* **87**, 877 (1987).
17. B. Lindman, P. Stilbs and M.E. Moseley, *J. Coll. Interf. Sci.* **83**, 569 (1981).
18. S.E. Friberg and P. Bothorel (Eds.), *Microemulsions: Structure and Dynamics*, CRC Press (Boca Raton, FL), 1987.
19. J. Prasilova and I. Burcova, *Radiochem. Radioanal. Lett.* **11**, 351 (1972).
20. V. Yatirajam, U. Ahuja and L.R. Kakkar, *Talanta* **23**, 819 (1976).
21. N.J. Clarke and S.H. Laurie, *J. Inorg. Biochem.* **12**, 37 (1980).
22. M.A. Hammer and A.G. Sykes, *Inorg. Chem.* **19**, 2881 (1980).
23. P.J. Aymonino, A.C. Ranade, E. Diemann and A. Muller, *Z. Anorg. Allgem. Chem.* **371**, 300 (1969).
24. A.E. Nielson, *Kinetics of Precipitation*, MacMillan, New York, 1964.
25. A. Veerbek, E. Gelade and F.C. De Schryver, *Langmuir* **2**, 448 (1986).
26. J.C. Railey and M. Buzier, *J. Coll. Interf. Sci.* **116**, 30 (1987).
27. J.B. Nagy, A. Gourgue and E.G. Derouane, *Stud. Surf. Sci. Catal.* **16**, 93 (1983).

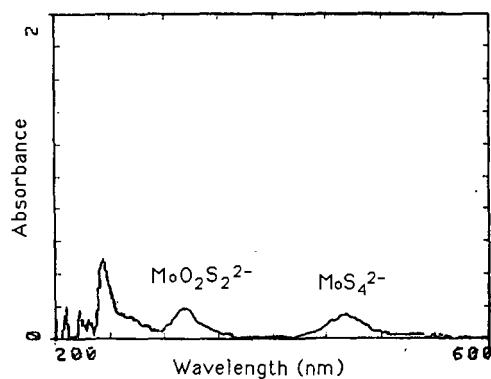


Figure 1. Absorption spectrum of 1×10^{-3} M thiomolybdate species in 0.1 M NP-5/cyclohexane/water microemulsion, $R=3$. (The concentration of the thiomolybdate species is with respect to the water pool volume.)

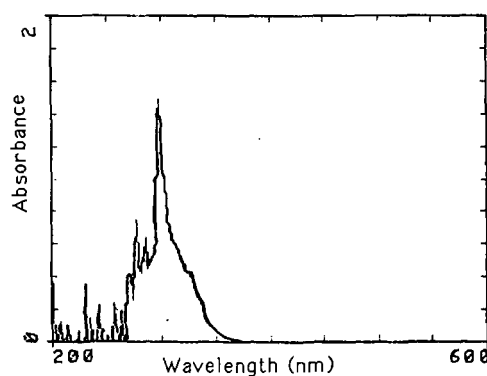


Figure 2. Absorption spectrum of molybdenum sulfide in 0.1 M NP-5/cyclohexane/water microemulsion, $R=6$, $[\text{MoS}_4^{2-}] = 1 \times 10^{-3}$ M. (The concentration of thiomolybdate species is with respect to the water pool volume.)

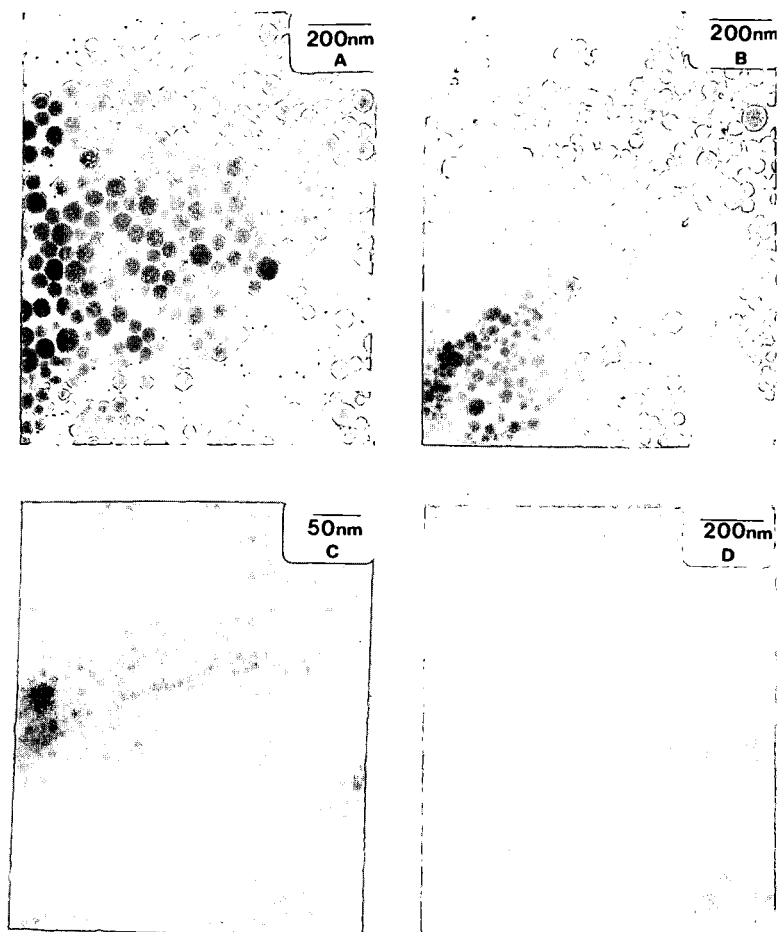


Figure 3. TEM micrographs of molybdenum sulfide particles prepared in 0.134 M NP-5/cyclohexane/water microemulsions: (A) $R=1$; (B) $R=1.5$; (C) $R=2$; (D) $R=3$.

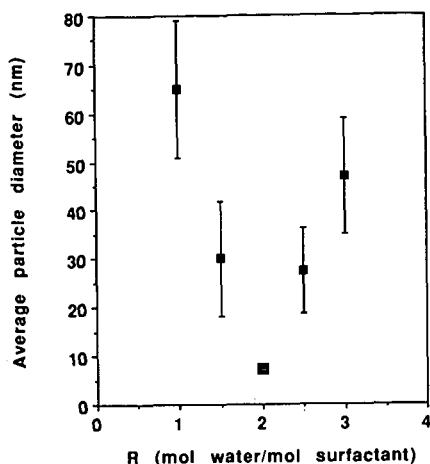


Figure 4. Effect of water-to-surfactant molar ratio (R) on average particle size for the 0.134 M NP-5/cyclohexane/water microemulsion. (The concentration of reactant species is constant with respect to the microemulsion.)



Figure 5. TEM micrograph of molybdenum sulfide prepared in 0.4 M NP-5/tetralin/benzyl alcohol microemulsion.

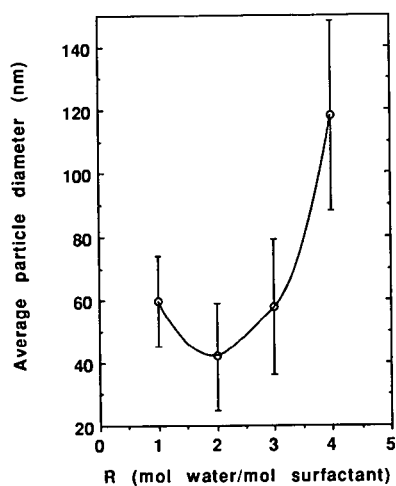


Figure 6. A plot of average particle diameter versus water-to-surfactant molar ratio (R) for the 0.4M NP-5/tetralin/benzyl alcohol microemulsion. The concentration of reactant species is constant with respect to the water pools.